Argonne National Laboratory

A PRACTICAL APPROACH TO
AVAILABILITY AND IRREVERSIBILITY

by

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I. INTRODUCTION

To the majority of engineers the Second Law of Thermodynamics is
a mysterious physical law that has yet to be disproved but which defies un-
derstanding. There is no denying that the Second Law is a difficult concept
to grasp, for, unlike the First Law, its development is based on mathemat-
ical inequalities, a nebulous property named entropy, and physically impos-
sible devices called reversible engines. It is not difficult to understand,
therefore, why an analytical technique named "Second Law Analysis" has
been shunned by all but a few. Fortunately, a tool as useful as the Second
Law Analysis will certainly become more popular as the mystery is
removed.

The purpose of this paper is to shed additional light on the tech-
niques of a Second Law Analysis. The stimulus for writing this paper
came from questions asked and difficulties that occurred during lectures
on the subject to students at the graduate level.

An excellent basic development of availability and irreversibility
equations is presented in a paper by Keenan[1] entitled Availability and
Irreversibility in Thermodynamics. Unfortunately, few engineers or pro-
fessors are aware of this work. The author believes that the concepts and
algebraic manipulations utilized in Keenan's derivation are readily followed
by the students but are not completely understood because of the students'
inability to relate some of the mathematical expressions with physical proc-
esses. This clearly manifests itself in the difficulties experienced by the
students while trying to apply the equations to a practical problem. The
difficulties arise because (1) the students fail clearly to define the sys-
tem or subsystem to which the analysis applies, and (2) they are unable to
define what forms of work should be included in the useful work term and
the maximum useful work term.

This paper utilizes Keenan's basic approach but presents the ma-
terial with emphasis upon a clear definition of the work associated with
each subsystem involved in the process. It is by this method that the stu-
dent can associate the concept or equation with something that has physical
meaning. As an example, this derivation does not utilize explicitly the
definition of the thermodynamic temperature scale, as did Keenan, but

uses instead the expression for the efficiency of a reversible engine. The students have used the efficiency equation, understand its significance, and have seen it represented graphically; therefore, it is easily accepted. Equations representing the irreversibility of a process are derived in terms of the various components of work which allow the irreversibilities resulting from friction and heat transfer to be separated and analyzed individually.

The first thing the students require is justification of the Second Law Analysis. "What can be done with the Second Law Analysis that can't be done with the First Law?" As pointed out by Keenan,[1] the generality of the Second Law is its main justification. Keenan says, "It is through this concept that processes as widely different as the decay of motion in a viscous fluid, the rectification of a binary mixture, and the dissociation of hydrogen peroxide can be examined from a common basis of comparison and their thermodynamic quality compared quantitatively by means of the irreversibility or a coefficient of performance as here defined."

The First Law provides a method for accounting quantitatively for the amounts of energy changed from one form to another or in transition between systems in the form of heat or work. The summary of such an energy balance is usually expressed in terms of heat and work required or produced and thermal efficiencies or coefficients of performance, depending upon whether the device or process produces or receives work.

The Second Law Analysis, on the other hand, provides a measure of the degree of sophistication of a device by comparing the work produced or received to that of an ideal device operating between the same initial and final states. The utility of the Second Law analysis is analogous to that of the property called entropy in that it provides a relative measure of quality rather than quantity. The summary of a Second Law Analysis is usually expressed in terms of irreversibilities and coefficients of performance.

The irreversibilities, as will be shown later, provide a quantitative measure of the loss of mechanically available energy that occurs when the performance of an actual device deviates from that of an ideal device. The coefficients of performance provide a measure of how closely the performance of an actual device approaches the performance of an ideal device with respect to work production or work requirements.

The First Law Analysis is usually sufficient for the users of a device, for they are primarily interested in the relative cost of the quantity of energy required to produce a unit of work, and this can be obtained from the thermal or mechanical efficiency. Those interested in the design and development of energy-converting devices could, however, use the Second Law Analysis as an effective tool in conjunction with the First Law Analysis. The Second Law Analysis, by pinpointing the location and magnitude

of useful energy losses, would be extremely valuable in directing the most profitable research and development effort.

The development of the available energy concept that has proved most successful for the author is presented below. The derivation is basically the same as that presented by Keenan[1] but with emphasis placed upon a careful definition of the work terms involved and upon designation of the system or subsystem being studied.

II. DERIVATION

Availability is defined[2] as "the maximum work which can result from the interaction of system and medium (atmosphere) when only cyclic changes occur in external things except for the rise of a weight." In this definition the system is assumed to include as much material and/or machinery as is affected by the process, with the exception of the atmosphere. The term atmosphere (or medium) in the above definition refers to an environment that is in its most stable state, and whose pressure and temperature are unaltered by any process executed by the system.

A. Availability of a Closed System

To evaluate the maximum useful work obtainable from the interaction of a system and the atmosphere, Keenan[1] proposed the model shown in Fig. 1. This model depicts a closed system, hereafter called the primary system, completely surrounded by a stable atmosphere at temperature T_0 and pressure p_0. The system exchanges heat only with the atmosphere and reacts with nothing else except an external, adiabatic device that either uses or provides energy in the form of work. For the interaction of the primary system and atmosphere to be completely reversible, that is, capable of producing the maximum useful work, it is necessary to postulate a cyclically operating reversible engine to provide for reversible heat transfer between the system and the atmosphere.
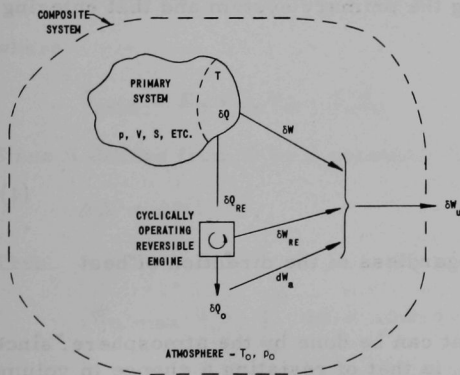

Fig. 1. Model of Closed System

The combination of the primary system, reversible engine, and atmosphere will hereafter be called the composite system.

The <u>actual</u> useful work done by the composite system during an expansion or contraction of the primary system is the algebraic sum of the primary system work, δW, the work of the postulated reversible engine, δW_{RE}, and the work done by the atmosphere during any volume change of the primary system, dW_a, or,

$$\delta W_u = \delta W + \delta W_{RE} + dW_a \quad . \tag{1}$$

The <u>maximum</u> useful work is obtained when the various components of work are derived from reversible processes. The reversible work done by the primary system may be expressed by

$$\delta W = \delta Q - dE \quad . \tag{2}$$

If it is recalled that the efficiency of a reversible engine may be expressed as

$$\eta_{RE} = (T - T_o)/T \quad ,$$

the work of the reversible engine equals

$$\delta W_{RE} = \delta Q_{RE} \frac{(T - T_o)}{T} \quad , \tag{3}$$

where δQ_{RE} represents the heat received by the reversible engine.

By virtue of the sign convention adopted for the accounting of energy, the relation between the heat leaving the primary system and that entering the reversible engine is

$$\delta Q_{RE} = -\delta Q \quad .$$

Thus, equation (3) becomes

$$\delta W_{RE} = -\delta Q \left(1 - \frac{T_o}{T}\right) \quad , \tag{4}$$

which is easily shown to be valid regardless of the direction of heat transfer.

The only reversible work that can be done by the atmosphere, since it is in a state of stable equilibrium, is that of resisting a change in volume at constant pressure, p_o:

$$dW_a = p_o dV_a \quad .$$

If the atmosphere is assumed to have fixed boundaries, then

$$dV_a + dV = 0 \quad ,$$

and

$$dW_a = -p_o \, dV \quad .$$ (5)

Substitution of the expressions for work, Eqs. (2), (4), and (5), into Eq. (1), and recall that for reversible processes

$$dS = \delta Q/T$$

result in an equation expressing the <u>maximum useful work</u> in terms of primary system properties and atmospheric temperature and pressure:

$$(dW_u)_{max} = dE + T_o dS - p_o dV \quad .$$

If a new quantity Φ is defined as

$$\Phi = E + p_o V - T_o S \quad ,$$

then

$$(dW_u)_{max} = -d\Phi \quad .$$

By definition, <u>availability</u> is the maximum useful work that can be done by a system, <u>in a given state</u>, while interacting only with an atmosphere, or

$$\text{Availability} \equiv \Lambda = \Phi - \Phi_{min} \quad ,$$

where

$$\Phi_{min} = E_o + p_o V_o - T_o S_o \quad .$$

Since Λ differs from Φ by a constant, Φ_{min}, it is obvious that

$$\Delta \Lambda = \Delta \Phi \quad .$$

Thus,

$$(W_u)_{max} = -\int_1^2 d\Phi = -\Delta \Phi = -\Delta \Lambda \quad ,$$

which says, in effect, the maximum useful work obtainable from a system-atmosphere combination during a <u>change of state</u> of the system is equal to the <u>change in availability</u> of the system-atmosphere combination.

B. Availability Change of a Closed System Receiving Heat from an External Reservoir

Many work-producing or -receiving devices require a transfer of heat between themselves and an energy reservoir with a temperature different from that of the atmosphere. For purposes of analysis this reservoir may be included in the primary system, in which case the total property changes of the system would include the property changes of the reservoir.

In many instances, however, it is more convenient to treat this energy source as an external heat reservoir. This convenience is easily seen if one considers the analysis of such energy-converting devices as gas turbines, internal combustion engines, and boilers, which require combustion to release the chemical energy in the fuel. Considering the combustion process to be an external energy reservoir that supplies heat at the combustion temperature simplifies the analysis by eliminating the thermodynamics of chemical reactions. Furthermore, the irreversibilities associated with the combustion process, losses about which little can be done, are not charged against the device being studied. This may be carried a step further by considering the energy reservoir to supply heat at the metallurgical temperature limit; thus, the cycle or process is not penalized by man's inability to develop suitable materials.

The maximum useful work obtainable from a system exposed to a heat reservoir in addition to an atmosphere may be evaluated by studying the model shown in Fig. 2.
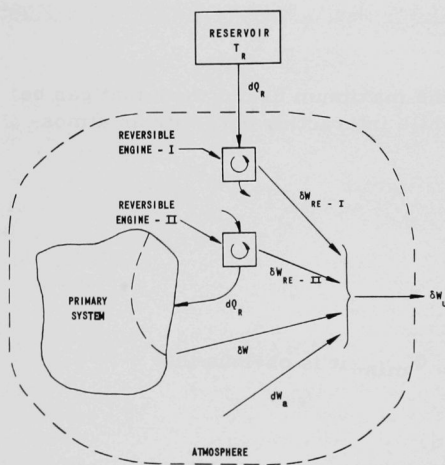
Fig. 2. Model of Closed System Receiving Heat from a Reservoir

The maximum work is obtained if reversible cyclic engines are used to transfer heat across finite temperature differences and if all other processes involved are reversible. It is not possible to transfer heat through an engine directly from the reservoir to the system because only a portion of the heat leaving the reservoir, dQ_R, would reach the system. However, a quantity of heat, dQ_R, can be made to go to the system, by utilizing two reversible cyclic

engines: reversible engine I transfers heat from the reservoir to the atmosphere while reversible engine II takes sufficient heat from the atmosphere to reject dQ_R to the system. Thus,

$$(dW_u)_{max} = dW_{RE-I} + \delta W_{RE-II} + \delta W + dW_a \quad . \tag{6}$$

The previous derivation shows, however, that the maximum useful work obtainable from a primary system exchanging heat only with the atmosphere through a reversible cyclic engine is equal to minus $d\Phi$. Thus,

$$\delta W_{RE-II} + \delta W + dW_a = -d\Phi \quad . \tag{7}$$

The work provided by reversible engine I equals

$$dW_{RE-I} = dQ_R \left(\frac{T_R - T_o}{T_R} \right) \quad , \tag{8}$$

where dQ_R is the heat received reversibly from the reservoir by the primary system. Combination of Eq. (7) and Eq. (8) with Eq. (6) gives an expression for the <u>maximum useful work of a system exposed to an atmosphere and receiving heat from an energy reservoir</u>:

$$(dW_u)_{max} = -d\Lambda = -d\Phi + dQ_R \frac{T_R - T_o}{T_R} \quad . \tag{9}$$

C. <u>Available Energy Associated with Flow across the Boundaries of</u> a <u>Control Volume</u>

When analyzing equipment or components which utilize flowing fluids, it is often more convenient to think in terms of a control volume (fixed volume) rather than a system (fixed mass). Therefore, it is desirable to derive the equations for maximum useful work as they relate to a control volume. Figure 3 represents a control surface σ through the boundaries of which flow a fluid or fluids and which exchanges heat only with the atmosphere. The material that was within σ at time t has moved to the position shown by the dashed lines in the time interval dt.

The rate of doing useful work as the fluid passes through σ is

$$\frac{(dW_u)_{max}}{dt} = \frac{-d\Lambda}{dt} = \frac{-d\Phi}{dt} \quad .$$
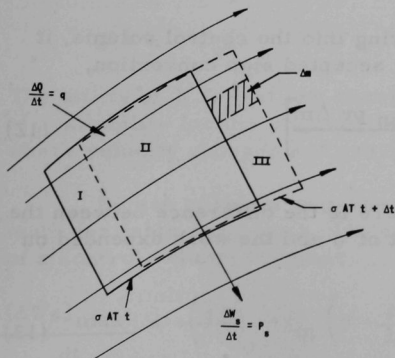

Fig. 3. Model of Control Volume

We see from Fig. 3 that the rate of change of availability is

$$\frac{\Delta \Lambda}{\Delta t} = \frac{(\Phi_{II} + \Phi_{III})_{t + \Delta t} - (\Phi_I + \Phi_{II})_t}{\Delta t} = \frac{(\Phi_{II})_{t + \Delta t} - (\Phi_{II})_t}{\Delta t}$$

$$+ \frac{\Sigma_{out} \phi \Delta m}{\Delta t} - \frac{\Sigma_{in} \phi \Delta m}{\Delta t} \quad .$$

In the limit as Δt approaches zero, region II becomes the space within the control volume σ, and the rate of change of availability may be written as

$$\frac{d\Lambda}{dt} = \left(\frac{\partial \Phi}{\partial t}\right)_{\sigma} + \Sigma_{out} \phi w - \Sigma_{in} \phi w \quad .$$

Thus, the rate of producing the maximum useful work, or the maximum useful power released, in the process is

$$\frac{(dW_u)_{max}}{dt} = (P_u)_{max} = - \left(\frac{\partial \Phi}{\partial t}\right)_{\sigma} + \Sigma_{in} \phi w - \Sigma_{out} \phi w \quad . \tag{10}$$

In general, when we have a device that utilizes a flowing fluid we are interested primarily in the "shaft work" (work delivered by a shaft, piston rod, electrical conductors, etc.) that can be delivered. The total useful work as expressed by Eq. (10) includes flow work done on or by the fluid element Δm in crossing σ plus the work done on or by the atmosphere (this assumes no fluid shear stresses at the point where fluid crosses the control surface). To derive equations in terms of maximum and actual shaft work, we must subtract the flow and atmosphere components of work from the total useful work, or

$$\frac{(dW_s)_{max}}{dt} = (P_s)_{max} = \frac{(dW_u)_{max} - dW_{flow} - dW_a}{dt} \quad . \tag{11}$$

If the fluid element, at pressure p, is flowing into the control volume, it must receive the flow work. Thus, by the accepted sign convention,

$$\frac{dW_{flow}}{dt} = \lim_{\Delta T \to 0} \left[\frac{\Sigma_{out} \, pv \, \Delta m - \Sigma_{in} \, pv \, \Delta m}{\Delta t} \right] \quad . \tag{12}$$

The net work done by the atmosphere is the difference between the work received while resisting the flow out of σ and the work expended on the inflow:

$$\frac{dW_a}{dt} = \Sigma_{in} \, p_0 vw - \Sigma_{out} \, p_0 vw \quad . \tag{13}$$

The general expression for the <u>maximum shaft work</u> obtainable from a control volume is obtained by substituting Eqs. (10), (12), and (13) into (11), or

$$\frac{(dW_s)_{max}}{dt} = (P_s)_{max} = -\left(\frac{\partial \Phi}{\partial t}\right)_\sigma + \Sigma_{in} \ (\phi + pv - p_ov)w$$

$$-\Sigma_{out} \ (\phi + pv - p_ov) \ w \quad . \tag{14}$$

Recall that

$$\phi \equiv e + p_ov - T_os \quad ,$$

that for a system in the absence of capillarity and external force fields other than gravity

$$e = u + \frac{c^2}{2g_c} + \frac{g}{g_c} \ z \quad ,$$

and that the enthalpy may be expressed as

$$h = u + pv$$

allows (14) to be written as

$$\frac{(dW_s)_{max}}{dt} = -\left(\frac{\partial \Phi}{\partial t}\right)_\sigma + \Sigma_{in} \left(h - T_os + \frac{c^2}{2g_c} + \frac{g}{g_c} \ z\right) w$$

$$-\Sigma_{out} \left(h - T_os + \frac{c^2}{2g_c} + \frac{g}{g_c} \ z\right) w \quad . \tag{15}$$

It is convenient at this point to define a new property

$$b \equiv h - T_os \quad .$$

The utility of b is that any change in this property represents the change of availability for the majority of steady-flow processes encountered, i.e., where velocity changes and gravitational forces are negligible.

By use of this new property, the general expression for the maximum available shaft work obtainable by virtue of flow across the surface of a control volume becomes

$$\frac{(dW_s)_{max}}{dt} = -\left(\frac{\partial \Phi}{\partial t}\right)_\sigma + \Sigma_{in} \left(b + \frac{c^2}{2g_c} + \frac{g}{g_c} \ z\right) w - \Sigma_{out} \left(b + \frac{c^2}{2g_c} + \frac{g}{g_c} \ z\right) w \quad .$$

If an energy reservoir outside of σ supplies an amount of heat dQ_R at temperature T_R to the fluid inside of σ, reasoning analogous to that used in obtaining Eq. (9) shows that the general experession for the maximum available shaft work becomes

$$\frac{(dW_s)_{max}}{dt} = -\left(\frac{\partial \Phi}{\partial t}\right)_\sigma + \Sigma_{in}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)w - \Sigma_{out}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)w$$
$$+ \frac{dQ_R}{dt}\left(\frac{T_R - T_o}{T_R}\right) \quad .$$

For most "semi-flow" processes it is easier to work with total changes rather than rates of change, and the above equation is generally more useful in the form

$$(dW_s)_{max} = -d\Phi_\sigma + \Sigma_{in}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)dm - \Sigma_{out}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)dm$$
$$+ dQ_R\left(\frac{T_R - T_o}{T_R}\right) \quad . \tag{16}$$

If steady flow conditions prevail, the state of the fluid at any point within the control volume must not change with time, or

$$d\Phi_\sigma = 0 \quad .$$

(This expression holds also for cyclically operating devices because Φ is a property.) The expression for the rate of change of availability (or the maximum useful shaft power) for a steady-flow system interacting with the atmosphere and receiving heat from an external reservoir then becomes

$$-\frac{d\Lambda}{dt} = (P_s)_{max} = \Sigma_{in}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)w - \Sigma_{out}\left(b + \frac{c^2}{2g_c} + \frac{g}{g_c}z\right)w$$
$$+ q_R\left(\frac{T_R - T_o}{T_R}\right) \quad .$$

III. IRREVERSIBILITY

The irreversibility of a process is defined as a quantitative measure of the loss of useful work suffered during the execution of the process. It is a measure of the deviation of the actual process from the ideal process.

Two types of equations are available for evaluating the irreversibility of a process. One type expresses the irreversibilities in terms of the

entropy change of all components affected by the process; the other expresses it as the difference between the maximum useful work (or power) and the actual useful work (or power). As pointed out by Keenan,[2] the equations utilizing the entropy changes are sometimes easier to use, but they do not show the nature of the irreversibility as clearly as do the equations utilizing the work terms. Both types of equations will be developed below.

A. Irreversibility in Terms of Work

A mathematical expression of irreversibility may be written as

$$I = \left(W_u\right)_{max} - W_u \quad , \tag{17}$$

$$= -\Delta\Lambda - W_u \quad . \tag{18}$$

The actual useful work differs from the availability change because of friction and heat transfer across finite temperature differences.

The frictional effects manifest themselves in two ways: as turbulence or shear work in a fluid, and as sliding or shear work in the bearings, cylinders, linkages, etc. Friction contributes to the irreversibility of a process by converting available energy, of a "high-grade" mechanical form, into heat, a "lower-grade" form of energy. Not all of the availability of the high-grade energy is lost, however, for if the heat that is generated is transferred to the atmosphere, a fractional amount $[1 - (T_o/T)]$ of the original available energy would be recovered. This "recovery" of available energy is the basic concept behind the reheat factor that is often used in turbine design.

Kiefer, Kinney, and Stuart[3] point out quite clearly that equations of a thermodynamic nature (energy balances) do not show the frictional effects explicitly, but that the frictional effects can be shown explicitly in equations of a mechanical nature (force balances). Thus, a dynamic analysis of an elementary mass of a flowing fluid which is producing shaft work results in the following equation:

$$\frac{g}{g_c} \, dz + \frac{cdc}{g_c} + \delta W_s = -vdp - \delta\psi \quad , \tag{19}$$

where $\delta\psi$ represents the frictional effects. The steady-flow energy equation, on the other hand, is written as

$$\frac{g}{g_c} \, dz + \frac{cdc}{g_c} + \delta W_s = -dh + \delta Q \quad . \tag{20}$$

An interesting relation is obtained by equating the right hand sides of Eqs. (19) and (20):

$$\delta Q = dh - vdp - \delta \psi$$

$$= de + pdv - \delta \psi \quad .$$

Comparison of this with the First Law written in terms of reversible processes:

$$\delta Q_{rev} = dh - vdp$$

$$= de + pdv$$

shows

$$\delta Q_{rev} = \delta Q + \delta \psi \quad . \tag{21}$$

If this is substituted into the definition of entropy:

$$dS = \frac{dQ_{rev}}{T} \quad ,$$

a general expression for entropy is obtained:

$$dS = \frac{\delta Q + \delta \psi}{T} \quad , \tag{22}$$

which shows mathematically that the entropy change is affected not only by the transfer of heat, but also by the presence of friction. The fact that the frictional term $\delta \psi$ is positive (always tends to increase the entropy) is easily established with the principle of the increase of entropy:

$$dS \geq \frac{\delta Q}{T} \quad .$$

Irreversibility in terms of work components may be obtained by substituting Eqs. (1), (2), (5), and (9) into

$$\delta I = (\delta W_u)_{max} - \delta W_u \quad ,$$

which gives

$$\delta I = \left[dQ_R \left(\frac{T_R - T_o}{T_R} \right) - d\Phi \right] - \left[\delta W_I + \delta W_{II} + \delta Q - dE - p_o dV \right]$$

$$= (max \; useful \; work) - (actual \; useful \; work) \quad .$$

Expanding $d\Phi$,

$$\delta I = d\, Q_R \left(\frac{T_R - T_o}{T_R}\right) - \delta W_I + T_o dS - \delta Q - \delta W_{II} \quad .$$

Substituting Eq. (22) for dS and regrouping give

$$\delta I = \left[dQ_R \left(\frac{T_R - T_o}{T_R}\right) - \delta W_I \right] + \left[-\left(\frac{T - T_o}{T}\right) \delta Q - \delta W_{II} \right] + \frac{T_o}{T} \,\, \delta\psi. \quad (23)$$

The terms in the brackets represent irreversibilities resulting from heat transfer, and the last term represents irreversibilities resulting from friction. Note that this equation shows that only a fraction of the frictional losses become unavailable. The terms δW_I and δW_{II} represent actual useful work obtained as the result of heat transfer. In most practical cases δW_I and δW_{II} would be zero. However, with the development of various thermoelectric devices the day may come when the useful work does not equal zero. Proper manipulation of the semi- and steady-flow availability equations gives equations identical in form with Eq. (23).

B. Irreversibility in Terms of Entropy for a Closed System

The First Law says that the _actual useful_ work that may come from the composite system shown in Fig. 1 is

$$W_u = \Delta E - \Delta E_a \quad , \tag{24}$$

since ΔE_I is zero for the cyclically operating engine. Substitution of Eq. (24) into Eq. (18) and recall that

$$\Delta V = -\Delta V_a$$

allows the irreversibility to be expressed as

$$I = T_o \Delta S + \Delta E_a + p_o \Delta V_a \quad ,$$

which may be reduced to

$$I = T_o (\Delta S + \Delta S_a) \quad . \tag{25}$$

When heat is transferred from a reservoir external to the primary system, the irreversibility for the system-reservoir combination becomes

$$I = -\Delta\Phi + Q_R \left(\frac{T_R - T_o}{T_R}\right) - W_u \quad . \tag{26}$$

The useful work of the composite system is

$$W_u = -\Delta E - \Delta E_a + Q_R \quad . \tag{27}$$

When Eq. (26) and (27) are combined and it is recalled that Q_R represents the heat received by the system from the reservoir (or $T_R \Delta S_R = -Q_R$), the irreversibility takes a form analogous to Eq. (25), i.e.,

$$I = T_o (\Delta S + \Delta S_a + \Delta S_R) \quad . \tag{28}$$

From Eqs. (25) and (28) it is seen that the irreversibility is equal to the net entropy change of all subsystems involved in the process multiplied by the absolute atmospheric temperature.

C. Irreversibility of Flow across a Control Surface

The irreversibility resulting from processes involving flow across the boundaries of a control volume may be written in terms of useful shaft work rather than total useful work:

$$\delta I = (dW_s)_{max} - \delta W_s \quad . \tag{29}$$

This equation is equivalent to Eq. (17) because, in the absence of fluid shear stresses at the control surface, the shaft work differs from the total useful work by the amount $(p - p_o) v \Delta m$.

An energy balance applied to the control volume pictured in Fig. 3 provides the following expression for the useful work done in an increment of time dt:

$$\delta W_s = -dE_\sigma + \Sigma_{in} \left(h + \frac{c^2}{2g_c} + \frac{g}{g_c} z \right) dm - \Sigma_{out} \left(h + \frac{c^2}{2g_c} + \frac{g}{g_c} z \right) dm$$

$$+ dQ_R - \delta Q_a \quad . \tag{30}$$

Substitution into Eq. (29) of the relation for $(dW_s)_{max}$, obtained by multiplying Eq. (15) by dt, and the expression for δW_s gives the irreversibility as

$$\delta I = -p_o dV_\sigma + T_o dS_\sigma + T_o [\Sigma_{out} sdm - \Sigma_{in} sdm] - \frac{T_o}{T_R} dQ_R + \frac{\delta Q_a}{T_o} \quad . \tag{31}$$

The first term on the right-hand side of Eq. (31) is zero because dV is zero for a control volume. The quantities $\delta Q_a/T_o$ and dQ_R/T_R may

be replaced by δS_a and $-dS_R$, respectively [the minus sign for dS_R is explained in the development of Eq. (28)]. Therefore, the general expression for the irreversibility of flow across a control surface becomes

$$\delta I = T_o [dS_\sigma + \Sigma_{out} \, sdm - \Sigma_{in} \, sdm + dS_R + \delta S_a] \quad . \tag{32}$$

D. Irreversibility in Steady Flow

For steady flow conditions the integrated form of (32), in terms of a unit mass of a single stream of fluid, is

$$I = T_o [S_2 - S_1 + \Delta S_R + \Delta S_a] \quad . \tag{33}$$

Again it is seen that the irreversibility is the product of T_o and the net entropy changes of the subsystems.

IV. COEFFICIENTS OF PERFORMANCE

Coefficients of performance provide a simple and convenient method for comparing the relative merits of different cycles or processes. Coefficients can be defined in a number of ways, most of which apply primarily to certain specific features or process. In general, it is desirable to have the coefficients vary from zero to one, and to equal one when the device is performing in an ideal manner.

For work producing cycles or devices, Keenan[1] has defined the coefficient of performance as

$$C_1 = W_u / (W_u)_{max} \quad ,$$

which approaches a value of one as the performance of the device approaches that of a reversible device. This may be seen if C_1 is expressed in terms of irreversibilities:

$$C_1 = 1 - \frac{I}{(W_u)_{max}} \quad .$$

For work-receiving devices, $(W_u)_{max}$ and W_u are less than zero and, in general, the absolute value of W_u is greater than $(W_u)_{max}$. Thus, a coefficient with the desired characteristics for work-receiving devices is

$$C_2 = (W_u)_{max} / W_u \quad ,$$

or

$$C_2 = 1 + \frac{I}{W_u} \quad .$$

V. DISCUSSION

Two types of equations that express irreversibilities are now available. The application of these equations to non-flow, semi-flow and steady-flow processes is given in the Appendix.

The student should be discouraged from using the equations involving entropy changes in the initial stages of study, particularly for problems in which the irreversibility is zero, because of their tendency to use "crutches," such as

$$dS_{isol} \geq 0 \quad ,$$

without truly understanding the physical significance of what they are doing. If the student is required to express, for the first few problems, the irreversibility in terms of the maximum and actual work done by the various components of the composite system, the entire concept becomes clearer. Furthermore, if the magnitude of the ΔS terms in the entropy-type irreversibility equations are compared with the magnitude of the various terms in the work-type equations, the significance of the ΔS terms soon becomes apparent, i.e., the student can now relate the entropy changes to physical processes.

An analysis of the irreversibility equations given by Keenan in reference (2):

$$dI = \left[\left(\frac{T - T_o}{T} \right) dQ - dW \right] - d\Phi \tag{34}$$

or

$$I = T_o \Delta S - T_o \int \frac{dQ}{T} \quad , \tag{34a}$$

reveals that these expressions account only for the frictional loss of the primary system; they do not account for irreversible heat transfer. This may be seen by substituting his definition of useful work

$$\delta W_u = \delta W - p_o dV$$

and expressions (2) and (31) into (34), which gives

$$\delta I = \frac{T_o}{T} \delta \psi \quad .$$

This is also readily seen in Eq. (34a) if a general expression for the entropy change Eq. (32) is utilized.

VI. CONCLUSIONS

Using the basic approach of Keenan,[1] but with emphasis placed upon recognition of the components of work supplied by the various parts of the composite system, equations were developed which expressed the change in availability and the magnitude of the irreversibility for non-flow, semi-flow, and steady-flow systems. The author believes that the concept of the Second Law Analysis becomes easier to grasp when the physically comprehensible work terms are stressed instead of the nebulous quantities normally associated with the Second Law.

Through use of the general expression for entropy change given in reference (3), the irreversibility equations were arranged to show specifically what portion of the losses come from friction and from irreversible heat transfer. It was further shown that the equations for irreversibility given in reference (2) do not account for irreversible heat transfer between the primary system and the atmosphere.

APPENDIX

The following examples are given to show the application of the preceding equations.

Closed System

Given: One pound of steam initially at 500°F is stirred at a constant pressure of 200 psia until $V_2 = 2V_1$. The atmosphere is at a pressure of 14.7 psia and a temperature of 60°F.

Calculate: The change in availability and the irreversibility associated with the process for the following cases: (a) adiabatic; (b) 75 Btu are lost to the atmosphere at a rate such that $\dfrac{\delta Q}{Q_{tot}} = \dfrac{dh}{h_2 - h_1}$.

Solution:

(a) Adiabatic

From the steam tables,

$h_1 = 1268.9$ Btu/lb

$S_1 = 1.6240$ Btu/lb-°R

$v_1 = 2.726$ ft^3/lb

$u_1 = 1168.0$ Btu/lb

$u_2 = h_2 - p_2 v_2 = 1528.3$ Btu/lb

$h_2 = 1730.2$ Btu/lb

$S_2 = 1.9642$ Btu/(lb)(°R)

$v_2 = 2v_1 = 5.452$ ft^3/lb

From Eq. (9) it is seen that the change in availability equals $\Delta \Phi$ since there is no heat transfer from an external reservoir ($dQ_R = 0$); therefore,

$$\Delta \Lambda = \Delta \Phi = \Delta U + p_o \Delta V - T_o \Delta S = 190.8 \text{ Btu} .$$

Obviously $\Delta\Lambda$ is the same for both the adiabatic and the heat transfer cases since Φ is a property of the system.

The irreversibility may be calculated from Eq. (23):

$$\delta I = \left[dQ_R \left(\frac{T_R - T_o}{T_R} \right) - \delta W_I \right] + \left[- \left(\frac{T - T_o}{T} \right) \delta Q - \delta W_{II} \right] + \frac{T_o}{T} \delta\psi \quad .$$

The first bracket equals zero because $dQ_R = 0$ and no useful work is obtained from reversible engine I (see Fig. 2). The second bracket equals zero for similar reasons; therefore,

$$I = \int_1^2 \frac{T_o}{T} \, d\psi \quad ,$$

which indicates all of the irreversibility is due to friction.

To evaluate $\delta\psi$ we may write the First Law as follows:

$$TdS = dU + p \, dV = \delta Q + \delta\psi \quad , \tag{A-1}$$

which reduces to

$$d\psi = du + pdv = dh \quad .$$

The integral of $(T_o/T)d\psi$ may be evaluated graphically from a plot of T_o/T vs h. This integration will yield

$$I = \int_1^2 \frac{T_o}{T} \, dh = 177 \text{ Btu} \quad .$$

The use of Eq. (25) gives the same answer much more rapidly, but does not provide the same insight into the nature of the irreversibility:

$$I = T_o \Delta S = 177 \text{ Btu} \quad .$$

(b) <u>75 Btu Heat Transfer</u>

The first bracket of Eq. (23) equals zero as before. Since there is heat transfer between the system and atmosphere, there is a potential for

obtaining some work. However, the actual work obtained is zero since the heat does not pass through a thermal converter of any type. Therefore,

$$I = -\int_1^2 \frac{T - T_0}{T} \delta Q + \int_1^2 \frac{T_0}{T} \delta \psi \quad .$$

Equation (A-1) shows

$$\delta \psi = dh - \delta Q \quad .$$

It was assumed that

$$\frac{\delta Q}{Q_{Total}} = \frac{dh}{h_2 - h_1} \quad ;$$

therefore, the frictional component of the irreversibility can be expressed as

$$\int_1^2 \frac{T_0}{T} \delta \psi = (h_2 - h_1 - Q) \int_1^2 \frac{T_0}{T} \frac{dh}{(h_2 - h_1)} \quad .$$

The graphical integration in part I gives

$$\int_1^2 \frac{T_0}{T} \frac{dh}{(h_2 - h_1)} = 0.383 \quad ,$$

and the irreversibility resulting from friction is

$$\int_1^2 \frac{T_0}{T} \delta \psi = (461.3 + 75)(0.383) = 205.7 \ \text{Btu/lb} \quad .$$

The irreversibility resulting from heat transfer is

$$\int_1^2 \frac{T - T_0}{T} \delta Q = Q(1 - 0.383) = 46.3 \ \text{Btu/lb} \quad .$$

The total irreversibility is

$$I = 46.3 + 205.7 = 252 \ \text{Btu/lb} \quad .$$

Once again it may be seen that Eq. (25) gives the answer with much less effort, e.g.,

$$I = T_o(\Delta S + \Delta S_a) = T_o \left[(0.3402) + \frac{75}{T_o} \right] = 252 \text{ Btu/lb} \quad ,$$

but it fails to reveal the source of the loss.

"Semi-flow" Problem

Given: A tank containing one pound of steam at 300 psia and 700°F is isolated from a cylinder and a frictionless piston by a valve. Initially, the volume between piston and cylinder is zero. A steady force is acting upon the piston such that a pressure of 100 psia is required to move the piston. The valve is opened slightly and steam flows into the cylinder slowly, until the pressure on the two sides of the valve equalizes. Assume the process to be adiabatic, $T_o = 530$ °R, and $p_o = 14.7$ psia.

Calculate:

(1) the change in availability of the steam upon entering the cylinder;

(2) the available energy in the steam that left the tank;

(3) the change in availability across the valve;

(4) the irreversibility associated with (a) the cylinder; (b) the valve; and (c) the steam leaving tank.

Solution: After the pressure has equalized at 100 psia, the conditions in the cylinder and tank are the following:

Cylinder	Tank
m = 0.571 lb steam	0.429 lb steam
T = 570°F	439°F
h = 1314.2 Btu/lb	1248.1 Btu/lb
u = 1202.5 Btu/lb	1151.9 Btu/lb
s = 1.7448 Btu/(lb)(°F)	1.6751 Btu/(lb)(°F)
v = 6.031 ft³/lb	5.197 ft³/lb

(1) The change in availability due to the processes in the cylinder is determined by reducing Eq. (16) to

$$\Delta \Lambda = \int_1^2 -d\Phi_{cyl} + (mb)_{in} = -54.41 \text{ Btu} \quad .$$

(2) The available energy in the steam leaving the tank equals

$$\Delta \Lambda = \int_0^{0.571} b_{out} \, dm = mh_{out} - mT_o s_{tank} = 243.48 \text{ Btu} \quad .$$

(3) The change in availability across the valve is evaluated from Eq. (16) reduced to the form

$$\Delta \Lambda = m \, b_{out} - \int_0^{0.571} b_{in} dm = -21.1 \text{ Btu} \quad .$$

(4a) The irreversibility of the process of steam entering the cylinder and raising the weight is

$$I = \int \frac{T_o}{T} \, \delta\psi = 0 \quad ,$$

since

$$\delta\psi = T \, ds \quad .$$

This shows that all of the available energy dissipated in the cylinder produced useful work.

(4b) The irreversibility resulting from the throttling of steam through the valve is

$$I = \int_{in}^{out} \frac{T_o}{T} \, \delta\psi = T_o \Delta S = 21.1 \text{ Btu} \quad .$$

(4c) The irreversibility associated with steam leaving the tank is

$$I = \int \frac{T_o}{T} \, \delta\psi = 0 \text{ Btu} \quad .$$

Steady-flow System

Given: An oil-fired furnace is to be used in conjunction with a nuclear reactor to superheat the steam and to preheat the feedwater in an economizer section. With a steam flow rate of 2.2×10^6 lb/hr, the terminal steam conditions are:

IN	OUT
P = 420 psia	370 psia
T = 449°F	1000°F

The feedwater flow rate is 1.97×10^6 lb/hr and the terminal conditions are:

	IN	OUT
P =	50 psia	50 psia
T =	193°F	213°F

The furnace releases 258 Mw of heat. The ambient temperature is 70°F and the allowable metallurgical temperature limit is 1200°F.

Calculate: (1) the total change in availability and (2) the irreversibility due to (a) friction in the superheater and (b) due to heat transfer.

Solution:

(1) The total change in availability per unit flow rate of steam is calculated from

$$\frac{\Delta\Lambda}{W_s\Delta t} = \Delta b_{steam} + \Delta b_{fw}\left(\frac{w_{fw}}{w_s}\right) - \frac{q_R}{w_s}\left(\frac{T_R - T_o}{T_R}\right) = -104.46 \text{ Btu/lb steam} \quad.$$

(2) The irreversibility associated with the heat-transfer processes is determined by reducing Eq. (23) to

$$I = Q_R\left(\frac{T_R - T_o}{T_R}\right) - \int_{steam}\left(\frac{T - T_o}{T}\right)Q - \int_{feedwater}\left(\frac{T - T_o}{T}\right)\delta Q \quad.$$

Graphical evaluation of the integrals after substituting dH for δQ yields the irreversibility due to heat transfer:

$$I_{H.T.} = 96.4 \text{ Btu/lb steam} \quad.$$

The irreversibility due to friction is

$$I = T_o\int\frac{\delta\psi}{T} = T_o\,\Delta S_s - T_o\int_{steam}\frac{dh}{T} = 9.86 \text{ Btu/lb steam} \quad.$$

The total irreversibility

$$I = 104.46 \text{ Btu/lb steam}$$

is easily checked by using Eqs. (18) or (32).

REFERENCES

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NOMENCLATURE

b   Defined property that is related to the available energy of a system with flowing fluids

c   Velocity of fluid streams

d   Denotes exact differential (a function of end states)

E   Total internal energy

e   Specific internal energy

g   Acceleration due to gravity

g_c Proportionality constant

h   Specific enthalpy

I   Irreversibility

m   Mass

P   Power

p   Pressure

Q   Quantity of energy in the form of heat

q   Rate of heat transfer

S   Total entropy

s   Specific entropy

T   Temperature

t   Time

u   Specific internal energy of a pure substance in the absence of motion, gravity, etc.

V   Total volume

v   Specific volume

W   Work

w   Flow rate

z   Elevation

Δ Indicates a finite increment

δ Inexact differential (not a function of end states)

η Efficiency

Λ Relative available energy

Φ Defined property that is proportional to the total available energy of an adiabatic primary system-atmosphere combination

ϕ Specific value of property defined above

Subscripts

a   Atmosphere

max   Maximum

min   Minimum

o   Refers to atmosphere in its most stable state

R   Reservoir

RE   Reversible engine

rev   Reversible

s   Shaft

σ Control volume

I & II   Postulated heat engines